(54) **Tapered block styrene/butadiene copolymers**

Styrolbutadienblockcopolymerisate mit Endblöcken von kontinuierlich sich ändernder Zusammensetzung

Copolymères à base de styrène et butadiène comprenant des blocs à séquences progressives

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EP-A- 0 026 916   **EP-A- 0 242 614**
EP-A- 0 436 225

EP 0 492 490 B1

Description

Background of the Invention

This invention relates to tapered block copolymers with vinylarene terminal blocks.

Polymerization of styrene and butadiene with organolithium initiators to produce block copolymers in which one or more non-elastomeric polymer blocks are bonded to one or more elastomeric polymer blocks has been disclosed. Similarly, styrene and butadiene with terminal tapered blocks have been prepared by sequential charging of initiator and monomers to the polymerization zone to produce block copolymers suitable for manufacture of transparent color-less packages, wrap, and like articles. EP-A-0 436 225 (to be considered under Article 54(3) EPC) and EP-A-0 242 614 disclose methods for preparing block copolymers by sequentially charging monomers and initiator in the polym-erization reaction. Since initiator is added at least three times, both documents refer to polymodal, at least trimodal block copolymers. There is a continuing need for transparent colorless material with good environmental stress crack resistance properties for packaging and related industries, especially in the food and medical packaging industry where large varieties of products are employed. It is essential in food packaging that the articles employed do not allow leakage or contamination of the product. A particularly difficult problem is encountered when the plastic containers are used for food products having oily bases such as butter, lard, margarine, cooking oil and salad dressing. The environ-mental stresses created by these oily bases often result in failure of the container.

Summary of the Invention

Thus, it is an object of this invention to provide a novel tapered block copolymer of conjugated dienes and vinyl-substituted aromatic hydrocarbons with improved environmental stress crack resistance.

A further object of this invention is to provide a novel process for making tapered block copolymers.

The inventive copolymers are prepared by the process as defined in claim 1.

Detailed Description of the Invention

The tapered block character of the polymer is produced by, after the two initial charges of monovinylaromatic monomer and initiator, charging with a blend of monovinylaromatic monomer and conjugated diene. This is generally but not always followed by a charge of monovinylaromatic monomer. Optionally, after the initial charges of monoviny-laromatic monomer and initiator, and before the reaction mixture is charged with the blend of monovinylaromatic mon-omer and conjugated diene, a charge of conjugated diene may be made. At each stage of charging, polymerization is allowed to continue until essentially no free monomer is present.

With each subsequent charge a different molecular weight species will be produced as well as the opportunity for polymerization of part of the charge with each of the existing species. After virtually complete polymerization of the final monomer charge, the active living linear block copolymers are charged with one or more terminating agents to form the desired polymodal tapered block copolymers.

Typical charging sequences with and without the optional charges and the major resulting polymer species at each stage, are shown in the following tables.

TABLE I

Typical Charging Sequence (a), (b), (d), (e)[a]		
Stage	Charge	Polymer Species[b]
1	initiator$_1$, tetrahydrofuran and styrene$_1$	S_1-Li_1
2	initiator$_2$ and styrene$_2$	S_1-S_2-Li_1 S_2-Li_2
3	butadiene$_1$ and styrene	S_1-S_2-B_1/S_3-Li_1 S_2-B_1/S_3-Li_2

[a](a), (b), (d), (e) correlate with steps in the summary of the invention.

[b]S = Styrene

B/S = Tapered block of butadiene and styrene.

TABLE I (continued)

Typical Charging Sequence (a), (b), (d), (e)[a]		
Stage	Charge	Polymer Species[b]
4	styrene$_4$	S_1-S_2-B_1/S_3-S_4-Li$_1$ S_2-B_1/S_3-S_4-Li$_2$

[a](a), (b), (d), (e) correlate with steps in the summary of the invention.
[b]S = Styrene
B/S = Tapered block of butadiene and styrene.

The subscript numbers indicate the order in which that particular component was charged or formed.

TABLE II

Typical Charging Sequence (a), (b), (c), (d), (e)[a]		
Stage	Charge	Polymer Species[b]
1	initiator$_1$, tetrahydrofuran and styrene$_1$	S_1-Li$_1$
2	initiator$_2$ and styrene$_2$	S_1-S_2-Li$_1$ S_2-Li$_2$
3	butadiene$_1$	S_1-S_2-B_1-Li$_1$ S_2-B_1-Li$_2$
4	butadiene$_2$ and styrene$_3$	S_1-S_2-B_1-B_2/S_3-Li$_1$ S_2-B_1-B_2/S_3-Li$_2$
5	styrene$_4$	S_1-S_2-B_1-B_2/S_3-S_4-Li$_1$ S_2-B_1-B_2/S_3-S_4-Li$_2$

[a](a), (b), (c), (d), (e) correlate with steps in the summary.
[b]S = Styrene
B/S = tapered block of butadiene and styrene.

The subscript numbers indicate the order in which that particular component was charged or formed.

At each stage, polymerization is allowed to continue until essentially no free monomer is present. The third and fourth steps shown above in the Table I charging sequence, and the third, fourth and fifth steps shown above in the Table II charging sequence are carried out in the absence of additional initiator.

Tapered blocks in each of the growing polymer chains present are produced by simultaneously charging both monomers in either the third or fourth step in the charging sequence. As can be seen from the intermediate products listed in the typical charging sequence tables above, there are at least two distinct polymer species present. Thus, essentially bimodal block copolymers comprising high and low molecular weight species are produced. The randomizer causes random polymerization of the monovinylaromatic monomer and the conjugated diene, but the diene still enters into the chain faster than the monovinyl substituted aromatic so that the block tapers gradually from an essentially polybutadiene segment, to a random copolymer segment, to an essentially monovinyl substituted aromatic segment.

The process of this invention can be carried out with any of the organomonoalkali metal compounds of the formula RM wherein R is an alkyl, cycloalkyl or arylcarbanion containing 4 to 8 carbon atoms and M is an alkali metal cation. The presently preferred initiator is n-butyllithium.

Suitable amounts of initiator in the first charge containing initiator are in the range from 0.008 to 0.045 parts per hundred parts total monomer, more preferably in the range from 0.01 to 0.035 parts per hundred parts total monomer, and most preferably in the range from 0.012 to 0.025 parts per hundred parts total monomer. Suitable amounts of initiator in the second charge containing initiator are in the range from 0.025 to 0.15 parts per hundred parts total monomer, more preferably in the range from 0.03 to 0.10 parts per hundred parts total monomer, and most preferably in the range from 0.035 to 0.08 parts per hundred parts total monomer.

The conjugated diene monomers which can be used contain 4 to 6 carbon atoms and include 1,3-butadiene, 2-methyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene and 1,3-pentadiene and mixtures thereof. Presently preferred is 1,3-butadiene.

The monovinylaromatic monomers which can be used contain 8 to 12 carbon atoms and include styrene, alpha-

methylstyrene, 4-methylstyrene, 3-methylstyrene, 2-methylstyrene, 4-ethylstyrene, 3-ethylstyrene, 2-ethylstyrene, 4-tert-butylstyrene and 2,4-dimethylstyrene and mixtures thereof. Presently preferred is styrene.

The polymerization process is carried out in a hydrocarbon diluent at any suitable temperature in a range of -10° to 150°C, preferably in the range of 0° to 120°C, at pressures sufficient to maintain the reaction mixture substantially in the liquid phase. Preferred hydrocarbon diluents include linear and cycloparaffins such as pentane, hexane, octane, cyclohexane, cyclopentane and mixtures thereof. Presently preferred is cyclohexane. Generally the temperature is such that the resulting polymer is in solution.

Small amounts of polar compounds are used in the hydrocarbon diluent to improve the effectiveness of alkylmono-alkali metal initiators such as n-butyllithium and to effect partial randomization of the vinylarene/conjugated diene so as to give a tapered block. Examples of polar compounds which can be advantageously employed are ethers, thioethers (sulfides) and tertiary amines. It is usually preferred to use ethers and sulfides in which the radicals attached to the oxygen or sulfur atoms are hydrocarbon radicals. Specific examples of such polar materials include dimethyl ether, diethyl ether, ethyl methyl ether, ethyl propyl ether, di-n-propyl ether, dibutyl ether, di-n-octyl ether, diethylglycol-dimeth-ylether, diethylglycol-diethylether, anisole, dioxane, 1,2-dimethoxyethane, dibenzyl ether, diphenyl ether, tetramethyl-ene oxide (tetrahydrofuran), dimethyl sulfide, diethyl sulfide, di-n-propyl sulfide, di-n-butyl sulfide, methyl ethyl sulfide, dimethylethylamine, tri-n-ethylamine, tri-n-propylamine, tri-n-butylamine, trimethylamine, triethylamine, N,N-di-methy-laniline, N-methyl-N-ethylaniline, and N-methylmorpholine. It is to be understood also that mixtures of these polar compounds can be employed in the practice of the present invention. Presently preferred are either tetrahydrofuran or diethyl ether. Amounts of randomizer to provide from 0.16 to 10 phm (parts per 100 parts of total monomer), preferably 0.25 to 1.0 phm are suitable.

The randomizer is added with the initial monovinylaromatic charge for the additional effect of causing the monovi-nylaromatic component resulting from each initiator charge to be of relatively narrow molecular weight distribution. Surprisingly, it has been found that superior results are obtained by having a bimodal molecular weight distribution of the total polymer chain lengths as a result of the addition of initiator two times and yet having the terminal monovinyl substituted aromatic component portions of the molecules resulting from each initiator addition to be of relatively narrow molecular weight distribution.

The polymerization is carried out in a substantial absence of oxygen and water, preferably under an inert gas atmosphere. Prior to termination of the reaction the reaction mass contains a very high percentage of molecules in which an alkali metal cation is positioned at one end of each polymer chain. Impurities in the feed such as water or alcohol reduce the amounts of monoalkali metal polymer in the reaction mass.

It is presently preferred to carry this reaction out without a coupling step employing coupling agents.

At the conclusion of the polymerization process the system is treated with an active hydrogen compound such as water, alcohols, phenols or linear saturated aliphatic mono- and dicarboxylic acids to remove lithium from the polymer chains and to deactivate any residual initiator that might be present. The polymer cement, i.e., the solution of the polymer in the polymerization solvent, can be treated in several methods in a post polymerization treatment. In one method, the polymer cement is contacted with a solution of a hindered phenolic antioxidant, generally a hydrocarbon solution thereof, then with water and carbon dioxide and finally with one or more stabilizers, if desired. Another suitable method comprises treating the polymer cement first with water and carbon dioxide and then with a hydrocarbon solution containing one or more appropriate stabilizers. A presently preferred stabilizer combination consists of a hindered phenol such as octadecyl 3-(3',5'-di-t-butyl-4'-hydroxy-phenyl) propionate (Irganox® 1076, Ciba-Geigy product) or tet-rakis [methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane (Irganox® 1010, Ciba-Geigy) and an organic phos-phite, preferably tris(nonylphenyl) phosphite (TNPP).

Examples of other suitable stabilizers include:

2,6-di-t-butyl-4-methylphenol,
1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) benzene, tris(3,5-di-t-butyl-4-hydroxybenzyl)isocyanu-rate,
tris(2,4-di-t-butylphenyl)phosphite, tris(mixed mono- and dinonylphenyl)phosphite,
2-t-butyl-α-(3-t-butyl-4-hydroxyphenyl)-p-cumenyl,
bis(p-nonyl-phenyl)phosphite,
2-t-butyl-6(3-t-butyl-5-methyl-2-hydroxybenzyl)4-methylphenyl acrylate, N,N-di(hydrogenated tallow) hydroxy-lamine and pentaerythritol tetrakis-3-laurylthiopropionate.

A typical charging sequence and ranges of amounts of the charges are given in Table III.

TABLE III

Typical Charging Sequence

Charge	Component	Broad Range	Preferred Range	Most Preferred Range
(a)	tetrahydrofuran initiator	0.16-10 phm[a] 0.008-0.045 phm (0.125-0.70 mhm)	0.20-2.0 phm 0.01-0.035 phm (0.16-0.55 mhm)	0.25-1.0 phm 0.012-0.025 phm (0.19-0.39 mhm)
	monovinylaromatic monomer	20-50 phm	25-45 phm	28-32 phm
(b)	initiator	0.015-0.15 phm	0.02-0.10 phm	0.035-0.08 phm
	monovinylaromatic monomer	5-25 phm	8-20 phm	10-15 phm
(c)	conjugated diene monomer	0-15 phm	3-14 phm	5-14 phm
(d)	conjugated diene monomer	10-40 phm	15-35 phm	20-30 phm
	monovinylaromatic monomer	10-40 phm	15-35 phm	20-30 phm
(e)	monovinylaromatic monomer	0-20 phm	4-15 phm	6-10 phm

[a] phm is parts per hundred parts total monomer.

The polymers prepared according to this invention are bimodal, resinous block copolymers and contain from 60

to 80, preferably from 65 to 80, and more preferably from 70 to 75, weight percent of polymerized monovinyl substituted aromatic hydrocarbon monomer based on the weight of total monomers employed.

The inventive copolymers contain from 20 to 40, preferably from 20 to 35, and more preferably from 25 to 30 weight percent conjugated diene monomer, based on the total weight of monomers incorporated into the copolymer.

The weight ratio of monovinyl substituted aromatic monomer to conjugated diene monomer in charge (d) is from 1:0.9 to 1:1.2, preferably from 1:1 to 1:1.1, and more preferably about 1:1.

Sufficient initiator is employed in both initiator charges to obtain a block copolymer having a melt flow ranging from 2 to 20 g/10 minutes as determined by ASTM D1238-73, condition G. Suitable amounts are described in Table III.

The following examples will describe in more detail the experimental process used and the polymodal internal tapered block copolymers with vinylarene terminal blocks obtained as a result of the process.

Example I

In each run there was prepared a resinous, linear bimodal block copolymer of styrene and 1,3-butadiene containing a polymerized internal tapered butadiene/styrene segment. The weight ratios of styrene to butadiene used in the copolymers were 85 to 15 and 75 to 25 as shown in Table III. While not wishing to be bound by theory, applicants believe the copolymers following the termination step are comprised primarily of species having at least the following general formulas:

S-S-taper-S

S-taper-S

wherein each S represents a polystyrene block and "taper" represents a random tapered block of polymerized styrene and butadiene.

Each polymerization run was carried out under nitrogen in a stirred, jacketed, stainless steel reactor of 7.6 ℓ of (two-gallon) capacity employing essentially anhydrous reactants and conditions. The block copolymers were prepared in a 4-step sequential charging process employing 2 n-butyllithium initiator charges, 3 styrene charges and 1 charge of a styrene/1,3-butadiene mixture. The total monomer charge in each run was 1600 grams. The total cyclohexane charge including that used for flushing lines was about 3400 grams (212 phm, where phm represents parts by weight cyclohexane per 100 parts by weight monomers). The following general charge order was used:

1. Cyclohexane diluent and tetrahydrofuran
2. n-butyllithium, first portion, about 2 weight percent in cyclohexane solvent
3. Styrene, first portion
4. n-butyllithium, second portion in cyclohexane solvent
5. Styrene, second portion
6. Styrene/butadiene mixture
7. Styrene, third portion
8. Terminating agent
9. Antioxidant in cyclohexane solution

Invention run 6 is detailed as an illustration of the actual procedure used.

In step 1, 170 phm cyclohexane; 0.3 phm tetrahydrofuran; 0.016 phm n-butyllithium; 30 phm styrene; and 14 phm cyclohexane diluent/flush were charged at about 43°C to the reactor. The temperature peaked at about 72°C as the styrene polymerized substantially adiabatically to completion in about 10 minutes. The reactor pressure was about 0.3MPa (30 psig).

In the second step, a second charge of 0.052 phm n-butyllithium, 12 phm styrene and 11.3 phm cyclohexane diluent/flush was added to the reactor, which was then about 55°C. The polymerization was allowed to proceed substantially adiabatically to completion in about 12 minutes, the temperature peaking at about 62°C. The reactor pressure was 0.4 MPa (40 psig).

In the third step, a mixture of 25 phm each of styrene and butadiene and 5.7 phm cyclohexane flush were added to the reactor, which was then about 52°C. The polymerization was allowed to proceed substantially adiabatically to completion in about 16 minutes with the temperature peaking at about 113°C. The reactor pressure was 0.52 MPa (60 psig).

In step four, 8 phm styrene and 5.7 phm cyclohexane flush were charged to the reactor which was then about 96°C. The reaction proceeded substantially adiabatically to completion in about 10 minutes with the temperature peaking at 99°C. The reactor pressure was 0.6 MPa (70 psig).

After polymerization was complete the reaction was terminated by the addition of about 0.28 phm water and 1.26

MPa (180 psi) carbon dioxide supplied from a 350 ml vessel equivalent to about 0.4 phm carbon dioxide and 5.7 phm cyclohexane flush. The reactor pressure was then 0.66 MPa (80 psig). After 20 minutes of reaction time and at a temperature of about 98°C, an antioxidant solution containing tris(nonylphenyl)phosphite (TNPP) and octadecyl 3-(3', 5'-di-t-butyl-4-hydroxyphenyl) propionate (Irganox 1076®) was added to the reactor charge. Sufficient solution was added to provide 1 phm TNPP and 0.25 phm Irganox 1076® while stirring continued. The reactor pressure was 0.98MPa (125 psig).

The polymer cement was transferred to a 18.9ℓ (5-gallon) capacity reactor where it was mixed with 0.25 phm microcrystalline wax (Be Square® 195) as an antiblocking agent. Be Square 195 wax is marketed by Bareco, a Division of Petrolite Corporation, Tulsa, Oklahoma.

The mixture was finally heated to about 178°C and flashed to remove a portion of the cyclohexane. Polymer isolated from this operation containing about 15-20 weight percent residual solvent can be dried further in a vacuum oven at about 100°C or passed through a devolatilizing extruder or the like to remove substantially all of the remaining solvent.

Following this general procedure a series of block copolymers employing various tetrahydrofuran levels and several styrene/butadiene weight ratios were prepared. The copolymers made and selected physical properties determined for them are given in Table IV.

The test specimens for the determination of physical properties other than environmental stress crack resistance (ESCR) were prepared by injection molding in an Arburg 221E/150, 0.0425 kg (1-1/2 ounce) machine at a barrel temperature of about 210°C, a mold temperature of about 23°C, a screw speed setting of about 360, an injection pressure adjusted to fill the mold, generally ranging from 5.86-6.90MPa (60-70 KP/cm^2) and a total cycle time of 45 seconds.

Test specimens for ESCR were cut from extruded sheet. The sheet was prepared by extruding the melt at a temperature of 175-185°C through a sheeting die and around a cooled polishing roll. The finished sheet, 0.03 to 0.05 cm (13 to 20 mils) in thickness, was then wound onto a 6.4 to 7.6 cm (21/2 - 3 inch) diameter tube and secured.

The results in Table IV show the effect of the THF level on the ESCR, hardness and flexural modulus properties of the copolymers. Invention run 1, with a THF level of 0.25 phm, gives a polymer that has an ESCR of 102 minutes in the puncture test. When the THF level is increased to 0.3 phm, the ESCR results are substantially better, as shown by the value of 142 minutes shown in invention run 2 and the value of 105 minutes shown in invention run 3.

TABLE IV

Effect of THF Level on Physical Properties of Linear Tapered Block Copolymers

Run No.	THF[a] phm[b]	Melt Flow g/10 min[c]	Hardness Shore D[d]	Flexural Modulus MPa[e]	Tensile Break MPa[f]	Elongation Break, %[g]	Izod Impact Notched, J/M[h]	ESCR,[i] minutes	Weight Ratio S/B	Remarks
1	0.25	6.1	66	1011	29.7	278	665	102.	75/25	invention
2	0.3	7.4	62	875	29.8	283	690	142.	75/25	invention
3	0.3	5.4	62	735	28.6	290	762	105.	75/25	invention

[a] THF is tetrahydrofuran.

[b] phm is parts by weight THF per 100 parts by weight monomers.

[c] ASTM D 238, condition G.

[d] ASTM D2240.

[e] ASTM D790.

[f] ASTM D638, 0.51 cm (0.2 inches)/minute.

[g] ASTM D638 0.51 cm (0.2 inches)/minute.

[h] ASTM D252.

[i] The values represent the minutes to failure in the puncture test described in Example III below, using soybean oil.

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Example II

Several resinous, linear, bimodal block copolymers of styrene and 1,3-butadiene, having a 70/30 weight ratio, and which contain an internal tapered styrene/butadiene segment and a polybutadiene segment were prepared in a five-step process. Two n-butyllithium charges were employed as recited in Example I. The copolymers, following termination, were believed to comprise primarily species having at least the following general formulas:

S-S-B-taper-S

S-B-taper-S

wherein S represents a polystyrene block, B represents a polybutadiene block, and "taper" represents a random tapered block of polymerized styrene and butadiene.

The polymerization was carried out as described in Example I except that butadiene was separately charged and polymerized after the polymerization of the second styrene charge and before polymerization of the styrene/butadiene portion. In invention run 1, 0.3 phm THF was present. The procedure actually employed in invention run 1 is given as an illustration.

In step 1, 170 phm cyclohexane; 0.3 phm THF; 0.016 phm NBL; 30 phm styrene; and 14 phm diluent/flush cyclohexane were charged at about 40°C to the reactor. The temperature peaked at about 71°C as the styrene polymerized substantially adiabatically to completion in about 12 minutes. The reactor pressure was 0.3MPa (30 psig).

In step 2, a second charge of 0.058 phm NBL, 12 phm styrene and 11.3 phm diluent/flush cyclohexane was added to the reactor which was then about 55°C. Polymerization proceeded substantially adiabatically to completion in about 13 minutes with the temperature peaking at about 65°C. The reactor pressure was 0.4MPa (40 psig).

In step 3, 12.5 phm butadiene and 5.7 phm cyclohexane flush were charged to the reactor which was then about 50°C. The step 3 charge polymerized substantially adiabatically to completion in about 16 minutes with the temperature peaking at about 68°C. The reactor pressure was about 0.4MPa (40 psig).

In step 4, 17.5 phm styrene, 17.5 phm butadiene and 5.7 phm cyclohexane flush were added to the reactor which was then about 66°C. Polymerization proceeded substantially adiabatically to completion in about 13 minutes with the temperature peaking at about 109°C. The reactor pressure was 0.52MPa (60 psig).

In step 5, 10.5 phm styrene and 5.7 phm cyclohexane flush were charged to the reactor which was then 94°C. Polymerization was allowed to proceed adiabatically to substantial completion in about 15 minutes with the temperature peaking at about 101°C. The reactor pressure was 0.6MPa (70 psig).

After polymerization was complete, the reaction was terminated, antioxidant solution added, wax added and the polymer recovered exactly in the manner described in Example I.

Selected physical properties of the copolymer were determined in the same manner as those obtained for the polymers prepared in Example I. The results are presented in Table V.

TABLE V

Physical Properties of Linear Tapered 70/30 Sytrene/Butadiene Copolymers

Run No.	THF[a] phm[b]	Melt Flow[c] g/10 min	Hardness[d] Shore D	Flexural Modulus[e] MPa	Tensile Break,[f] MPa	Elongation Break,[g] Percent	Izod Impact Notched, J/M[h]	ESCR,[i] minutes	Remarks
1	0.3	5.5	58	799.8	28.6	287	585	186	invention

[a] THF is tetrahydrofuran.

[b] phm is parts by weight THF per 100 parts by weight monomers.

[c] ASTM D1238, condition G.

[d] ASTM D2240.

[e] ASTM D790.

[f] ASTM D638, 0.51 cm (0.2 inches)/minute.

[g] ASTM D638, 0.51 cm (0.2 inches)/minute.

[h] ASTM D252.

[i] The values represent the minutes to failure in the puncture test described in Example III below, using soybean oil.

Example III

A portion of each of the polymers produced in runs 1,2 and 3 shown in Table IV was tumbled with 40 weight percent general purpose (crystal) polystyrene, such as, for example, Styron 555, a product of The Dow Chemical Company, Midland, Michigan. The resulting blends consisting of 60 weight percent block copolymer and 40 weight percent crystal polystyrene were extruded and formed into sheets 0.03 to 0.05 cm (13 to 20 mils) thick as before and then wound onto 6.4 to 7.6 cm (2 1/2-3 inch) tubes and secured. Specimens were cut from each roll and tested for environmental stress crack resistance by means of a test developed for that purpose. The test is based upon the breaking of a small square of a 0.04 cm (15 mil) plastic sheet with a weighted stainless steel rod with a rounded tip. The samples were cut into 5.08 cm (two-inch) squares and the thickness of each was measured. Each sample was then placed over a hole in a test bed and clamped down with a rubber ring and weight. Four drops of the test solution (soybean oil) were placed on the sample directly over the hole. The weighted stainless rod with a rounded tip was placed on the sample and a timer was triggered. All samples were measured ten times and the results were reported with statistical relevance. All samples were compared to a control run under the same test conditions.

For the control sample the break time for the puncture test (curlup) was 3.89 minutes, with a 95% confidence limit of 0.18 minute.

A portion of the polymer produced in run 1, shown in Table V, was mixed with 50 weight percent of the crystal polystyrene, extruded to form sheet and wound onto tubes in the manner previously described. Specimens for ESCR testing were cut from the roll.

The amount of THF employed in each polymerization run, a brief indication of polymer structure for the high molecular weight fraction of the total polymer, the quantity of monomers charged and the ESCR results obtained are presented in Table VI.

The ESCR results in runs 1 through 3 with the 75/25 styrene/butadiene block copolymers and in run 4 with the 70/30 styrene/butadiene block copolymers follow the same trend shown in Tables IV and V for the copolymers alone. That is, as the THF level employed in polymerisation is increased, the ESCR value also increases. The best results are apparent at the 0.3 phm THF level.

The styrene/butadiene weight ratio in all the blends was 85/15. However, run 4 employed 50 weight percent polystyrene in the blend. Runs 1 through 3 were made with 40 weight percent polystyrene. The results suggest that when the crystal polystyrene content comprises about 50 weight percent or more of the blend, the effect of using more THF during polymerization of the block copolymer is largely negated.

TABLE VI

Block Copolymer/Polystyrene Blends					
Run No.	Block Copolymer Structure	Styrene/Butadiene Weight Ratio		THF[b] phm[c]	ESCR,[d] minutes[e]
	Monomer Charged, phm[a]	Copolymer	Blend		
1	S,S,B/S,S(30, 12, 25/25, 8)	75/25	85/15	0.25	4.0
2	S,S,B/S,S(30, 12, 25/25, 8)	75/25	85/15	0.3	6.6
3	S,S,B/S,S(30, 12, 25/25, 8)	75/25	85/15	0.3	8.3
4	S,S,B/S,S(30, 12, 12.5, 17.5/17.5, 10.5)	70/30	85/15	0.3	1.8

[a]phm is parts by weight per 100 parts total monomer.

[b]THF is tetrahydrofuran.

[c]phm is parts by weight THF per 100 parts by weight monomers.

[d]ESCR is environmental stress crack resistance.

[e]The values represent minutes until failure in the puncture test described in Example III above, using soybean oil.

Claims

1. A process for making tapered block copolymers, characterized by the sequential steps of

(a) charging a monovinylaromatic monomer, a randomizer and an initiator,

(b) charging additional monovinylaromatic monomer and initiator,

(c) optionally charging a conjugated diene monomer,

(d) charging a mixture of monovinylaromatic monomer and conjugated diene monomer, and

(e) optionally charging additional monovinylaromatic monomer,

wherein in each of steps (a) to (e) polymerization is conducted until essentially no free monomer is present, and said initiator additions in step (a) and step (b) represent the only initiator additions during the course of said process, wherein the process comprises at least one of said steps (c) and (e).

2. The process of claim 1 consisting of steps (a), (b), (d) and (e).

3. The process of claim 1 consisting of steps (a), (b), (c), (d) and (e).

4. The process of claim 1 consisting of steps (a), (b), (c) and (d).

5. The process of any of the preceding claims wherein said monovinylaromatic monomer contains 8 to 12 carbon atoms and said conjugated diene contains 4 to 6 carbon atoms, said monomers being introduced at a ratio of 60 to 80 weight percent monovinylaromatic monomer and 20 to 40 weight percent conjugated diene monomer, thus giving a resinous block copolymer.

6. The process of any of the preceding claims wherein said randomizer in step (a) is present in an amount in the range from 0.16 to 10 parts per hundred parts total monomer.

7. The process of any of the preceding claims wherein the weight ratio of monovinylaromatic monomer to conjugated diene monomer in step (d) is within the range of 1:0.9 to 1:1.2.

8. The process of any of the preceding claims wherein said monovinylaromatic monomer charged in step (a) is from 20 to 50 parts, preferably from 25 to 45 parts and most preferably from 28 to 32 parts, each per hundred parts total monomer charged in said process.

9. The process of any of the preceding claims wherein said monovinylaromatic monomer charged in step (b) is from 5 to 25 parts, preferably from 8 to 20 parts and most preferably from 10 to 15 parts, each per hundred parts total monomer charged in said process.

10. The process of any of claims 1 and 3 to 9 wherein said conjugated diene monomer charged in step (c) is from greater than 0 to about 15 parts, preferably from 3 to 14 parts and most preferably from 5 to 14 parts, each per hundred parts total monomer charged in said process.

11. The process of any of the preceding claims wherein said monovinylaromatic monomer charged in step (d) is from 10 to 40 parts, preferably from 15 to 35 parts and most preferably from 20 to 30 parts, each per hundred parts total monomer charged in said process.

12. The process of any of the preceding claims wherein said conjugated diene monomer charged in step (d) is from 10 to 40 parts, preferably from 15 to 35 parts and most preferably from 20 to 30 parts, each per hundred parts total monomer charged in said process.

13. The process of any of claims 1, 2, 3 and 5 to 12 wherein said additional monovinylaromatic monomer charged in step (e) is from greater than 0 to about 20 parts, preferably from 4 to 15 parts and most preferably from 6 to 10 parts, each per hundred parts total monomer charged in said process.

14. The process of any of the preceding claims wherein said conjugated diene monomer is 1,3-butadiene, said monovinylaromatic monomer is styrene, said organomonoalkali metal initiator is n-butyllithium, and said randomizer is tetrahydrofuran.

15. The process of any of the preceding claims wherein said polymerization is carried out in a hydrocarbon diluent; wherein said polymerization is carried out in a substantial absence of oxygen and water at temperatures ranging from -10 °C to 150 °C; wherein, after said polymerization is substantially complete, the system is treated with a

terminating agent and then a stabilizer; and wherein, after termination with said terminating agent, a portion of remaining hydrocarbon diluent is flashed off.

16. The process of claim 15 wherein said terminating agent is water and carbon dioxide; and wherein said stabilizer is chosen from hindered phenols and organophosphites.

Patentansprüche

1. Verfahren zur Herstellung von konischen Blockcopolymeren, gekennzeichnet durch folgende aufeinanderfolgende Stufen:

(a) Beschicken mit einem monovinylaromatischen Monomeren, einem Randomisierungsmittel und einem Initiator,
(b) Beschicken mit weiterem monovinylaromatischem Monomeren und Initiator,
(c) ggf. Beschicken mit einem konjugierten Dien-Monomeren,
(d) Beschicken mit einem Gemisch aus monovinylaromatischem Monomerem und konjugiertem Dien-Monomerem und
(e) ggf. Beschicken mit zusätzlichem monovinylaromatischem Monomerem,

wobei die Polymerisation in den einzelnen Stufen (a) bis (e) so lange durchgeführt wird, bis im wesentlichen kein freies Monomeres mehr vorhanden ist, und wobei die Initiatorzugaben in Stufe (a) und Stufe (b) die einzigen Initiatorzugaben im Verfahrensverlauf darstellen, wobei das Verfahren mindestens eine der Stufen (c) und (e) umfaßt.

2. Verfahren nach Anspruch 1, bestehend aus den Stufen (a), (b), (d) und (e).

3. Verfahren nach Anspruch 1, bestehend aus den Stufen (a), (b), (c), (d) und (e).

4. Verfahren nach Anspruch 1, bestehend aus den Stufen (a), (b), (c) und (d).

5. Verfahren nach einem der vorstehenden Ansprüche, wobei das monovinylaromatische Monomere 8 bis 12 Kohlenstoffatome enthält und das konjugierte Dien 4 bis 6 Kohlenstoffatome enthält, wobei die Monomeren in einem Verhältnis von 60 bis 80 Gew.-% monovinylaromatischem Monomeren und 20 bis 40 Gew.-% konjugiertem Dien-Monomerem zugeführt werden, wodurch man ein harzartiges Blockcopolymeres erhält.

6. Verfahren nach einem der vorstehenden Ansprüche, wobei das Randomisierungsmittel in Stufe (a) in einer Menge im Bereich von 0,16 bis 10 Teilen pro 100 Teile der gesamten Monomeren vorhanden ist.

7. Verfahren nach einem der vorstehenden Ansprüche, wobei das Gewichtsverhältnis des monovinylaromatischen Monomeren zum konjugierten Dien-Monomeren in Stufe (d) im Bereich von 1:0,9 bis 1:1,2 liegt.

8. Verfahren nach einem der vorstehenden Ansprüche, wobei die Menge des in Stufe (a) zugegebenen monovinylaromatischen Monomeren 20 bis 50 Teile, vorzugsweise 25 bis 45 Teile und insbesondere 28 bis 32 Teile, jeweils pro 100 Teile der gesamten, im Verfahren zugegebenen Monomeren, beträgt.

9. Verfahren nach einem der vorstehenden Ansprüche, wobei die Menge des in Stufe (b) zugegebenen monovinylaromatischen Monomeren 5 bis 25 Teile, vorzugsweise 8 bis 20 Teile und insbesondere 10 bis 15 Teile, jeweils pro 100 Teile der gesamten, im Verfahren zugegebenen Monomeren, beträgt.

10. Verfahren nach einem der Ansprüche 1 und 3 bis 9, wobei die Menge des in Stufe (c) zugegebenen konjugierten Diens mehr als 0 bis etwa 15 Teile, vorzugsweise 3 bis 14 Teile und insbesondere 5 bis 14 Teile, jeweils pro 100 Teile der gesamten, im Verfahren zugegebenen Monomeren, beträgt.

11. Verfahren nach einem der vorstehenden Ansprüche, wobei die Menge des in Stufe (d) zugegebenen monovinylaromatischen Monomeren 10 bis 40 Teile, vorzugsweise 15 bis 35 Teile und insbesondere 20 bis 30 Teile, jeweils pro 100 Teile der gesamten, im Verfahren zugegebenen Monomeren, beträgt.

12. Verfahren nach einem der vorstehenden Ansprüche, wobei die Menge des in Stufe (d) zugegebenen konjugierten Dien-Monomeren 10 bis 40 Teile, vorzugsweise 15 bis 35 Teile und insbesondere 20 bis 30 Teile, jeweils pro 100 Teile der gesamten, im Verfahren zugegebenen Monomeren, beträgt.

13. Verfahren nach einem der Ansprüche 1, 2, 3 und 5 bis 12, wobei die Menge des in Stufe (e) zugegebenen zusätzlichen monovinylaromatischen Monomeren mehr als 0 bis etwa 20 Teile, vorzugsweise 4 bis 15 Teile und insbesondere 6 bis 10 Teile, jeweils pro 100 Teile der gesamten, im Verfahren zugegebenen Monomeren, beträgt.

14. Verfahren nach einem der vorstehenden Ansprüche, wobei es sich beim konjugierten Dien-Monomeren um 1,3-Butadien handelt, beim monovinylaromatischen Monomeren es sich um Styrol handelt, beim organomonoalkalimetall-Initiator es sich um n-Butyllithium handelt und beim Randomisierungsmittel es sich um Tetrahydrofuran handelt.

15. Verfahren nach einem der vorstehenden Ansprüche, wobei die Polymerisation in einem Kohlenwasserstoff-Verdünnungsmittel durchgeführt wird; wobei die Polymerisation insbesondere im wesentlichen in Abwesenheit von Sauerstoff und Wasser bei Temperaturen im Bereich von -10°C bis 150°C durchgeführt wird; wobei nach im wesentlichen vollständiger Polymerisation das System mit einem Abbruchmittel und anschließend mit einem Stabilisator behandelt wird; und wobei nach Abbruch mit dem Abbruchmittel ein Teil des verbleibenden Kohlenwasserstoff-Verdünnungsmittels rasch abgedampft wird.

16. Verfahren nach Anspruch 15, wobei es sich beim Abbruchmittel um Wasser und Kohlendioxid handelt; und wobei der Stabilisator unter sterisch gehinderten Phenolen und Organophosphiten ausgewählt wird.

Revendications

1. Un procédé pour fabriquer des copolymères séquences à séquences progressives, caractérisé par les étapes séquentielles consistant à :

(a) charger un monomère monovinylaromatique, un agent de randomisation et un amorceur,
(b) charger un monomère monovinylaromatique supplémentaire et un amorceur,
(c) charger éventuellement un monomère diénique conjugué,
(d) charger un mélange de monomère monovinylaromatique et de monomère diénique conjugué, et
(e) charger éventuellement un monomère monovinylaromatique additionnel, dans lequel dans chacune des étapes (a) à (e), la polymérisation est mise en oeuvre jusqu'à ce qu'essentiellement aucun monomère libre ne soit présent, et lesdites additions d'amorceur dans l'étape (a) et l'étape (b) représentent les seules additions d'amorceur pendant le déroulement dudit procédé,

dans lequel le procédé comprend au moins une desdites étapes (c) et (e).

2. Le procédé selon la revendication 1 comprenant les étapes (a), (b), (d) et (e).

3. Le procédé selon la revendication 1 comprenant les étapes (a), (b), (c), (d) et (e).

4. Le procédé selon la revendication 1 comprenant les étapes (a), (b), (c) et (d).

5. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit monomère monovinylaromatique renferme 8 à 12 atomes de carbone et ledit diène conjugué renferme 4 à 6 atomes de carbone, lesdits monomères étant introduits selon un rapport de 60 à 80 % en poids de monomère monovinylaromatique et de 20 à 40 % en poids de monomère diénique conjugué, ce qui donne un copolymère séquencé résineux.

6. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit agent de randomisation dans l'étape (a) est présent selon une quantité comprise dans la gamme de 0,16 à 10 parties pour 100 parties de monomère total.

7. Le procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport pondéral du monomère monovinylaromatique au monomère diénique conjugué dans l'étape (d) se situe dans la gamme de 1:0,9 à 1:1,2.

8. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit monomère monovinylaro-

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matique chargé dans l'étape (a) représente de 20 à 50 parties, de préférence de 25 à 45 parties et mieux encore de 28 à 32 parties, chaque partie étant pour cent parties de monomère total chargé dans ledit procédé.

9. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit monomère monovinylaromatique chargé dans l'étape (b) représente de 5 à 25 parties, de préférence de 8 à 20 parties et mieux encore de 10 à 15 parties, chaque partie étant pour cent parties de monomère total chargé dans ledit procédé.

10. Le procédé selon l'une quelconque des revendications 1 et 3 à 9, dans lequel ledit monomère diénique conjugué chargé dans l'étape (c) représente plus de 0 à environ 15 parties, de préférence de 3 à 14 parties et mieux encore de 5 à 14 parties, chaque partie étant pour cent parties de monomère total chargé dans ledit procédé.

11. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit monomère monovinylaromatique chargé dans l'étape (d) représente de 10 à 40 parties, de préférence de 15 à 35 parties et mieux encore de 20 à 30 parties, chaque partie étant pour cent parties de monomère total chargé dans ledit procédé.

12. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit monomère diénique conjugué chargé dans l'étape (d) représente de 10 à 40 parties, de préférence de 15 à 35 parties et mieux encore de 20 à 30 parties, chaque partie étant pour cent parties de monomère total chargé dans ledit procédé.

13. Le procédé selon l'une quelconque des revendications 1, 2, 3 et 5 à 12, dans lequel ledit monomère monovinylaromatique supplémentaire chargé dans l'étape (e) représente plus de 0 à environ 20 parties, de préférence de 4 à 15 parties et mieux encore de 6 à 10 parties, chaque partie étant pour cent parties de monomère total chargé dans ledit procédé.

14. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit monomère diénique conjugué est le 1,3-butadiène, ledit monomère monovinylaromatique est le styrène, ledit amorceur de métal organomonoalcalin est le n-butyllithium et ledit agent de randomisation est le tétrahydrofuranne.

15. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ladite polymérisation est mise en oeuvre dans un diluant hydrocarboné, dans lequel ladite polymérisation est mise en oeuvre en l'absence essentielle d'oxygène et d'eau à des températures comprises dans la gamme de -10°C à 150°C ; dans lequel après que ladite polymérisation est essentiellement terminée, le système est traité avec un agent de terminaison et ensuite un agent stabilisant et dans lequel après la terminaison avec ledit agent de terminaison, une partie du diluant hydrocarboné restant est séparée par distillation.

16. Le procédé selon la revendication 15, dans lequel ledit agent de terminaison est l'eau et le dioxyde de carbone et dans lequel ledit stabilisant est choisi parmi les phénols à empêchement et les organophosphites.